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THE GENERAL CONDITIONS OF VALIDITY OF THE
PRINCIPLE OF LE CHATELIER.

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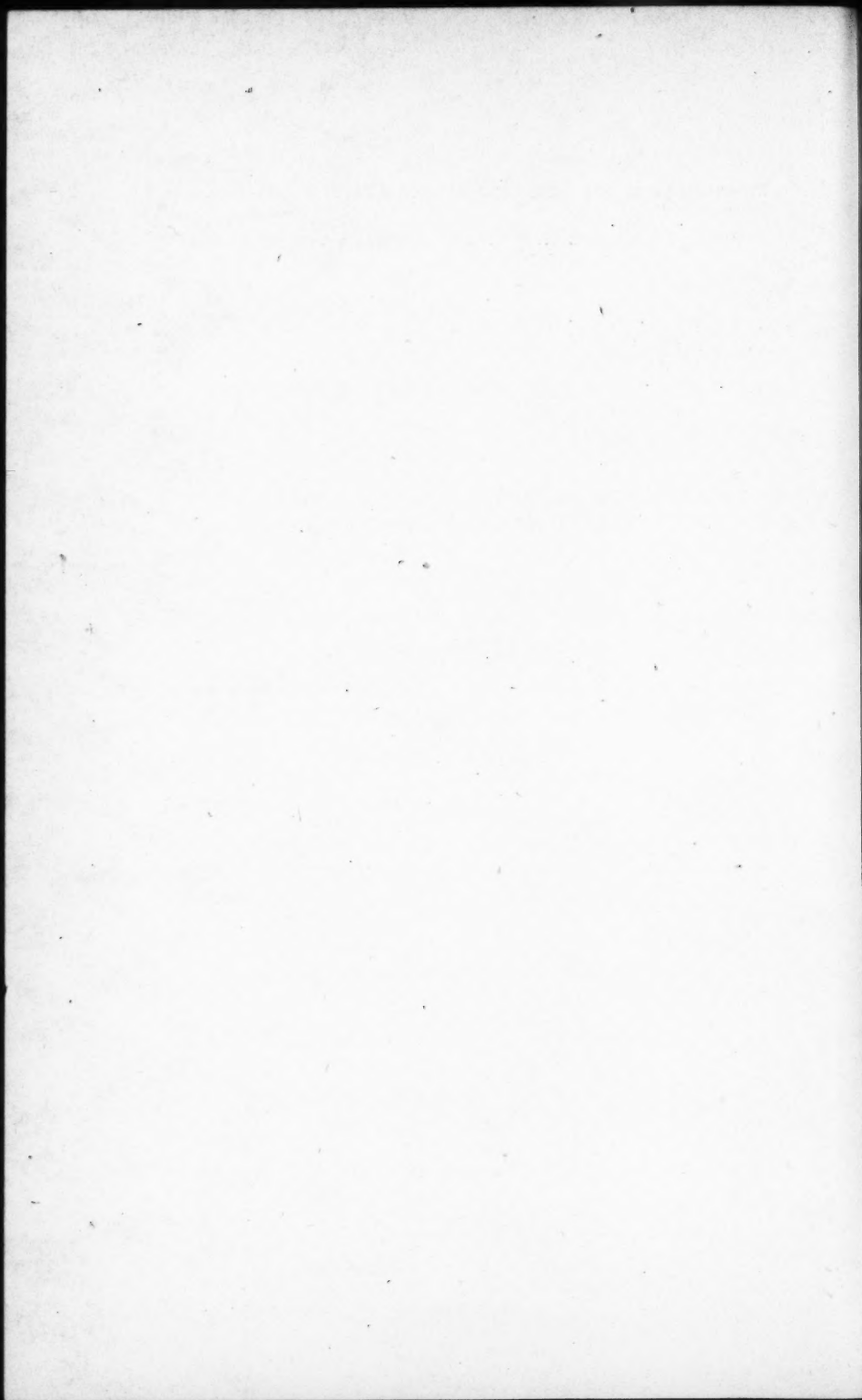


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THE GENERAL CONDITIONS OF VALIDITY OF THE PRINCIPLE OF LE CHATELIER.¹

BY ALFRED J. LOTKA.

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Presented by Raymond Pearl.

THE derivation of the principle of Le Chatelier from the laws of thermodynamics is familiar.

We may approach a converse problem. What, in the broadest terms, are the conditions which a system must satisfy in order that the principle shall apply to it? The interest of this problem arises from the fact that we have reason to suspect these conditions may prove broader than the domain within which the laws of thermodynamics are conveniently applicable.² We may therefore expect that a satisfactory solution of the converse problem may enable us to make rigorous application of the principle to systems to which, from lack of sufficient data it may be impossible, or from other causes it may be inconvenient to apply thermodynamic methods.

Consider a system whose state is defined in terms of a variable x and a parameter G . The system is one of that class, the history of which follows a law

$$\frac{dx}{dt} = f(x, G) \quad (1)$$

(For example, it may consist of a mixture of $(A_1 - 2x)$ mols H_2O vapor, $(A_2 + 2x)$ mols of hydrogen, and $(A_3 + x)$ mols of oxygen at 2000 deg. C. in a rigid enclosure of volume G ; A_1, A_2, A_3 being constants, namely initial masses). It is understood that other parameters besides G may enter into the function f , but it is unnecessary to set them forth explicitly, since in the reflections which follow only

¹ Papers from the Department of Biometry and Vital Statistics, School of Hygiene and Public Health, Johns Hopkins University, No. 37.

² See Ehrenfest, *Zeitschr. für phys. Chem.* 1911, vol. 77, pp. 227, 244; Wolchonsky, *Jl. Russ. Phys. Chem. Soc.*, 1912, vol. 44, pp. 305, 310; Chwolson, *Lehrbuch der Physik*, 1909, vol. 3, p. 547; Bancroft, *Jl. Am. Chem. Soc.*, 1911, p. 92; Fournier d'Albe, *Contemporary Chemistry*, 1911, p. 38; Löwy, *Kosmos*, 1911, p. 331; Le Dantec, *La Stabilité de la Vie*, 1910, p. 25; L. Fredericq, *Arch. de Zool. Exp. et Gén.*, ser. 2, vol. 3, 1885, p. XXV; Spencer, *First Principles*, chapter 22, section 173, Burt's Edition, p. 433. For further historical and bibliographic notes see Duhem, *Traité d'Énergétique*, 1911, vol. 1, pp. 523, 524.

changes in x and in one parameter G at a time will be considered, the other parameters being constant.

According to (1) a stationary state (which need not be a true equilibrium in the thermodynamic sense) is defined by

$$0 = \frac{dx}{dt} = f(x_1, G) \quad (2)$$

where x_1 denotes the equilibrium value of x .

If the parameter G is altered by a small increment δG , the corresponding increment δx_1 in the equilibrium value x_1 of x is, in view of (2), given by

$$\frac{\partial f}{\partial x} \delta x_1 + \frac{\partial f}{\partial G} \delta G = 0 \quad (3)$$

$$\frac{\delta x_1}{\delta G} = - \frac{\partial f / \partial G}{\partial f / \partial x} \quad (4)$$

1. STABLE STATE.

If the stationary state defined by (2) is stable, we must have in the neighborhood of that state³

$$\frac{\partial f}{\partial x} < 0 \quad (5)$$

We can then distinguish two cases:

a.) $\frac{\partial f}{\partial G} > 0$. This means that the parameter G is one whose increase accelerates the transformation the progress of which is measured by x . In this case it follows immediately from (4) that $\frac{\delta x_1}{\delta G} > 0$. In other words, if the system is stable in the stationary state defined by (2), then increasing a parameter which accelerates the transformation will shift the position of the stationary state in the direction of increased transformation. From this alone, however, it does not necessarily follow that the new stationary state will actually become

³ Condition (5) states that the velocity $f = \frac{\partial f}{\partial x} \delta x$ is always opposite in sign to the (small) displacement δx from equilibrium. This is evidently necessary for stability of equilibrium.

established. But, starting from the stationary state, at which $\frac{dx}{dt} = f = 0$, increase in G leads to a positive value of f . That is to say, a change actually takes place with a velocity directed towards the new stationary state, i.e. increased x .

b.) $\frac{\partial f}{\partial G} < 0$; i.e. increase in the parameter G retards the transformation. Here it follows by similar reasoning that increase in G shifts the position of the stationary state towards diminished transformation. Furthermore, in this case the increment δG initiates a retrograde change, i.e. a change toward the new stationary state.

In both cases, (1.a) and (1.b), therefore, a change δG in the parameter G is followed by a transformation δx_1 towards the new stationary state, in the direction of the influence of the parameter G upon the velocity of transformation.

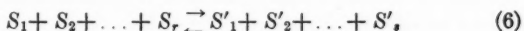
2. UNSTABLE STATE.

Consider now the case in which $\frac{\partial f}{\partial x} > 0$. The stationary state defined by (2) is then unstable. A train of reasoning precisely analogous to that set forth above leads, in this case, to the conclusions:

(1) A change δG in the parameter G determines a shift of the stationary state in the direction opposed to the influence of the parameter G upon the transformation.

(2) The system, disturbed from existing stationary state by a change δG , moves, not towards, but away from the new stationary position.

Application to Influence of Initial Masses. Consider a transformation



Let $\xi_1, \xi_2, \dots, \xi_r$ be the masses (expressed in mols) at time t of the components S_1, S_2, \dots, S_r ; similarly let $\xi'_1, \xi'_2, \dots, \xi'_s$ be the masses of S'_1, S'_2, \dots, S'_s .

Let x measure the progress of the transformation from left to right, and let $p_i x$ be the amount (in mols) of S_i transformed from time $t = 0$ to time $t = t$.

Let A_i be the initial value of the mass (in mols) of some component

S_i which disappears in the transformation when x increases, and let A'_i be the initial value of some component S'_i which appears in the same transformation.

We have, according to (4),

$$\frac{\delta x_i}{\delta A_i} = - \frac{\partial f}{\partial A_i} / \frac{\partial f}{\partial x} \quad (7)$$

If we are dealing with a system of constant mass, we have an equation of constraint

$$m_1 \xi_1 + m_2 \xi_2 + \dots = m_1 A_1 + m_2 A_2 + \dots \quad (8)$$

where m_1, m_2, \dots are the molecular weights of the substances S_1, S_2, \dots . From (8) we find by differentiation

$$\frac{\partial \xi_i}{\partial A_i} = 1 \quad (9)$$

so that we may write, instead of (7),

$$\frac{\delta x_i}{\delta A_i} = - \frac{\partial f}{\partial \xi_i} / \frac{\partial f}{\partial x} \quad (10)$$

From (10) it is seen that $\frac{\delta x_i}{\delta A_i}$ and $\frac{\partial f}{\partial \xi_i}$ are always of the same sign provided $\frac{\partial f}{\partial x}$ is negative, i.e., provided that the system is stable in the

equilibrium defined by $f = 0$. That is to say, if the system is stable, and if adding a quantity of a component disappearing in the transformation increases the velocity of the transformation (at the previous equilibrium), then such addition will shift the equilibrium in the direction of increased transformation. In this case, then, the principle of Le Chatelier holds good.

On the contrary, by similar reasoning, it is found that if the addition of a quantity of a particular substance disappearing in the transformation retards the transformation, the principle does not hold as regards that substance.

Again, by similar reasoning, it is found that the principle holds or does not hold, according as the addition of a substance S'_i appearing in the transformation retards or hastens the transformation. We may therefore summarize the facts as follows:

1. Given that the system, at equilibrium, is stable with regard to changes in x , and that there is a relation of the type (8), an "equation of constraint" connecting the masses ξ and their initial values A , then the condition which must be satisfied in order that the Le Chatelier Principle may hold with regard to the effect of a change in the initial mass of some *one* component, is that the addition of such component shall accelerate or retard the transformation (at equilibrium), according as such component disappears or appears in such transformation.

2. Given that the conditions for the validity of the Le Chatelier Principle stated under (1) are satisfied for each and every component, then it is easily shown that the system is necessarily stable with regard to changes in x , so that the condition of such stability with regard to changes in x is automatically satisfied and does not need to be expressly stated. For, if $\frac{\partial f}{\partial A_i} > 0$ for every component which disappears in the transformation, and if $\frac{\partial f}{\partial A'_i} < 0$ for every component which appears, then, in view of (9), the same is true of $\frac{\partial f}{\partial \xi_i}$ and $\frac{\partial f}{\partial \xi'_i}$.

But

$$d\xi_i = -p_i dx \quad (11)$$

$$d\xi'_i = +p'_i dx \quad (12)$$

where p_i, p'_i are positive numbers, and

$$\frac{df}{dx} = \sum \frac{\partial f}{\partial \xi_i} \frac{d\xi_i}{dx} + \sum \frac{\partial f}{\partial \xi'_i} \frac{d\xi'_i}{dx} \quad (13)$$

$$= - \sum \frac{\partial f}{\partial \xi_i} p_i + \sum \frac{\partial f}{\partial \xi'_i} p'_i \quad (14)$$

which is necessarily a negative quantity if

$$\frac{\partial f}{\partial \xi_i} > 0, \quad \frac{\partial f}{\partial \xi'_i} < 0 \quad (15)$$

3. It should be noted that the argument by which our conclusions have been drawn depends on the existence of equations of constraint, relations such as (8), connecting the ξ 's and the A 's. In the absence

of such constraints we are in no wise assured that the principle holds.⁴ This must be clearly borne in mind in seeking to apply the Le Chatelier principle, for example, to biological systems. Thus, for instance, the malaria equilibrium under the conditions contemplated by Sir Ronald Ross,⁵ is independent of the initial amount of malaria in the system (provided only this is not zero). This state of affairs arises out of the fact that there is no equation of constraint of type (8), in this case, connecting the initial amount of malaria with its status at any subsequent epoch.

Case of more than one variable. A somewhat more complicated case arises if the system under consideration is susceptible of several concurrent transformations, so that its state at any instant requires for its definition not one variable x , but a number of such variables.

It will suffice if we consider here the case for two variables x, y , as, for example, the case of a pair of consecutive reversible reactions



In this case we have

$$\frac{dx}{dt} = f_1(x, y, G) \quad (18)$$

$$\frac{dy}{dt} = f_2(x, y, G) \quad (19)$$

and equilibrium is defined by

$$f_1 = f_2 = 0 \quad (20)$$

Differentiating, in a manner analogous to that followed in the case of a single variable x , we have

$$\frac{\partial f_1}{\partial x} \delta x_1 + \frac{\partial f_1}{\partial y} \delta y_1 + \frac{\partial f_1}{\partial G} \delta G = 0 \quad (21)$$

$$\frac{\partial f_2}{\partial x} \delta x_1 + \frac{\partial f_2}{\partial y} \delta y_1 + \frac{\partial f_2}{\partial G} \delta G = 0 \quad (22)$$

⁴ For there is then no necessary relation between ξ and A , so that the derivative $\frac{\partial f}{\partial A}$ is no longer equal to $\frac{\partial f}{\partial \xi}$, but is indeterminate or meaningless.

⁵ "The Prevention of Malaria," Second English Edition, John Murray, London, 1911, p. 679; Lotka, *Nature*, Feb. 1912, p. 497.

a system of linear equations, which we solve for $\frac{\delta x_1}{\delta G}$, $\frac{\delta y_1}{\delta G}$ and obtain

$$\frac{\delta x_1}{\delta G} = - \frac{\begin{vmatrix} \frac{\partial f_1}{\partial G} & \frac{\partial f_1}{\partial y} \\ \frac{\partial f_2}{\partial G} & \frac{\partial f_2}{\partial y} \end{vmatrix}}{\begin{vmatrix} \frac{\partial f_1}{\partial x} & \frac{\partial f_1}{\partial y} \\ \frac{\partial f_2}{\partial x} & \frac{\partial f_2}{\partial y} \end{vmatrix}} \quad (23)$$

and a similar expression for $\frac{\delta y_1}{\delta G}$.

Condition of Stability. A general solution of (18), (19) can be written ⁶ in the form of exponential series

$$x = P_0 + P_1 e^{\lambda_1 t} + P_2 e^{\lambda_2 t} + P_{11} e^{2\lambda_1 t} + \dots \quad (24)$$

$$y = Q_0 + Q_1 e^{\lambda_1 t} + Q_2 e^{\lambda_2 t} + Q_{11} e^{2\lambda_1 t} + \dots \quad (25)$$

where $\lambda_1 \lambda_2$ are the roots of

$$\Delta(\lambda) = \begin{vmatrix} \left(\frac{\partial f_1}{\partial x} - \lambda \right) & \frac{\partial f_1}{\partial y} \\ \frac{\partial f_2}{\partial x} & \left(\frac{\partial f_2}{\partial y} - \lambda \right) \end{vmatrix} = 0 \quad (26)$$

The condition for stability ⁷ of the equilibrium is that the real parts of all the roots λ are negative. This in turn demands that the absolute term $\Delta(0)$ be positive. But this absolute term is, evidently,

$$\Delta(0) = \begin{vmatrix} \frac{\partial f_1}{\partial x} & \frac{\partial f_1}{\partial y} \\ \frac{\partial f_2}{\partial x} & \frac{\partial f_2}{\partial y} \end{vmatrix} \quad (27)$$

⁶ A. J. Lotka, Proc. Am. Ac., 1920, p. 139.

⁷ Idem, loc. cit., p. 144; Hurwitz, Math. Ann., 1875, vol. 46, p. 521; Blondel, Jl. de Physique, 1919, pp. 117, 153.

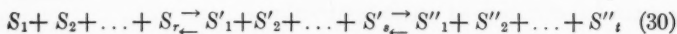
so that we must have, for stability,

$$\begin{vmatrix} \frac{\partial f_1}{\partial x} & \frac{\partial f_1}{\partial y} \\ \frac{\partial f_2}{\partial x} & \frac{\partial f_2}{\partial y} \end{vmatrix} > 0 \quad (28)$$

In consequence, given stability of equilibrium, the sign of $\frac{\partial x_1}{\partial G}$ will be the same as that of the numerator in (23), i.e., that of the expression

$$\frac{\partial f_1}{\partial G} \frac{\partial f_2}{\partial y} - \frac{\partial f_2}{\partial G} \frac{\partial f_1}{\partial y} = D \quad (29)$$

Example. Consecutive Reactions. By the way of example we may apply these results to the case of a pair of consecutive reversible reactions.



Let x denote the progress of the first reaction from left to right (so that, for example, a quantity, $p_t x$ of the substance S_i has been transformed at time t); and let y similarly denote the progress of the second reaction, from left to right.

Let us consider the effect upon x_1 , the equilibrium value of x , of an increment $\delta A''_k$ in the initial amount of substance S''_k appearing as product of the second reaction.

We have, according to (23)

$$\frac{\delta x_1}{\delta A''_k} = - \frac{\begin{vmatrix} \frac{\partial f_1}{\partial A''_k} & \frac{\partial f_1}{\partial y} \\ \frac{\partial f_2}{\partial A''_k} & \frac{\partial f_2}{\partial y} \end{vmatrix}}{\begin{vmatrix} \frac{\partial f_1}{\partial x} & \frac{\partial f_1}{\partial y} \\ \frac{\partial f_2}{\partial x} & \frac{\partial f_2}{\partial y} \end{vmatrix}} \quad (31)$$

We shall assume stability, so that the denominator is positive. In the numerator, evidently ⁸

⁸ If we exclude any possible catalytic influence.

$$\frac{\partial f_1}{\partial A''_k} = 0 \quad (32)$$

so that this numerator reduces to

$$\frac{\partial f_2}{\partial A''_k} \cdot \frac{\partial f_1}{\partial y} \quad (33)$$

Stability demands

$$\frac{\partial f_1}{\partial y} > 0 \quad (34)$$

On the other hand the principle of Le Chatelier would make

$$\frac{\partial x_1}{\partial A''_k} < 0 \quad (35)$$

This, by (31), in view of (32), (33), (34), will be true or not according as

$$\frac{\partial f_2}{\partial A''_k} < 0 \quad (36)$$

Hence the principle of Le Chatelier holds good or not, as applied to the effect of A''_k upon x_1 , according as

$$\frac{\partial f_2}{\partial A''_k} < 0 \quad (37)$$

From this point on the discussion would follow essentially similar lines as in the case of a single dependent variable; it is therefore unnecessary to carry this out in further detail.

Influence of External Factors. We have hitherto tacitly assumed that (1), or (18), (19) are the only conditions for equilibrium, or, that, if there are any other conditions to be satisfied, these are in some way automatically taken care of.

In point of fact, in general, in addition to a condition of the form

$$\frac{dx}{dt} = f(x, G) \quad (1)$$

there will be further conditions of the form

$$H = H_e \quad (38)$$

where H is a parameter entering into the function f , while H_e is a parameter defining certain "external conditions." For example, H may be the pressure exerted by a gaseous mixture against an enclosure, and H_e may be the external pressure applied to a movable piston

forming part of that enclosure. Here it is not enough, for complete equilibrium, that (1) be satisfied, but (38) also must hold.

Furthermore, the conditions (1) and (38) define equilibrium, but are insufficient to determine its stability, since they give us no information regarding the behavior of the system when $H \neq H_e$, i.e. when not in equilibrium with the external parameter H_e .

In order to settle this point we must have some further data. We are here interested in systems in which such additional data are furnished in the following manner:

In the case of these systems it is found that, in relation to the parameter G a certain parameter H having certain peculiar properties, can be defined by a relation.

$$\varphi(\xi_1, \xi_2, \dots, G, H) = \text{constant} \quad (39)$$

or its equivalent

$$\Psi(x, A_1, A_2, \dots, G, H) = \text{constant} \quad (40)$$

The peculiar property of G referred to above is as follows

$$\frac{dG}{dt} \begin{matrix} > \\ < \end{matrix} 0 \text{ according as } H - H_e \begin{matrix} > \\ < \end{matrix} 0 \quad (41)$$

It will perhaps be well, before proceeding any farther, to illustrate this by a concrete example. Consider the system



If ξ_1 is the mass of H_2O expressed in mols, ξ'_1 the mass of H_2 and ξ'_2 the mass of O_2 similarly expressed; if V is the volume (parameter G) and if P is the pressure (parameter H) exerted upon the enclosure, then the equation (39) here takes the form

$$PV = (\xi_1 + \xi'_1 + \xi'_2) R\theta \quad (43)$$

where θ is the absolute temperature and R the general gas constant. Or, if A_1, A'_1, A'_2 are the initial masses of H_2O, H_2 and O_2 respectively, (expressed in mols), and x measures the progress of the reaction, as, for example, by the number of O_2 mols formed, then evidently

$$\xi_1 = A_1 - 2x \quad (44)$$

$$\xi'_1 = A'_1 + 2x \quad (45)$$

$$\xi'_2 = A'_2 + x \quad (46)$$

so that (40) takes the form

$$\begin{aligned} PV &= \{(A_1 - 2x) + (A'_1 + 2x) + (A'_2 + x) R\theta \\ &= \{(x + A_1 + A'_1 + A'_2) R\theta \end{aligned} \quad (47)$$

In this case it is quite evident that the parameters P, V (corresponding to H, G of the general case) have the property defined by (41), which here appears as the characteristic property of the intensity factor and the capacity factor of an energy.

But for our present purposes we are not concerned with the question whether or not the parameters G, H defined for a given system are or are not factors of an energy. We must be prepared to deal with cases where this is either uncertain or actually known not to be true. All we need to know, for our purpose, is that the parameters G, H have the property defined by (41). An example may serve to illustrate the fact that this property may be shared by physical quantities not obviously related to energy.

Among the parameters on which the rate of increase of a human population depends is the area a occupied by them, since this determines the population density, which in turn influences the death rate in well-known manner,⁹ and, presumably, in some degree the birth rate also.

Now there is an obvious relation between population density and ground rent. Regulation is effected about as follows: There is a certain demand for space, a desire for expansion, which may be measured by the rent H per unit area that the individual is willing to pay. On the other hand there is a certain market price H_e which must be paid to obtain accommodation. Now if $H > H_e$, i.e. if, on an average, an individual is willing to pay more than the market price, the population will spread over a greater area by renting more ground. If, on the other hand $H < H_e$ the individual is not willing to pay the market price, he will retrench, he will move from a six room apartment to a five room apartment say, and the area occupied by the population will contract. The parameter H_e functions, in fact, much like a "surface pressure," tending to compress the population into a smaller area. The most striking exhibition of this "surface-pressure" is seen in a great metropolis such as New York, where the population, a naturally two-dimensional structure spread like a film over the earth's surface, has been thrown into great creases towering 700 feet and more, 50 layers deep, above the street level.

⁹ See, for example, Newsholme, *Vital Statistics*, 1899, p. 154.

forming part of that enclosure. Here it is not enough, for complete equilibrium, that (1) be satisfied, but (38) also must hold.

Furthermore, the conditions (1) and (38) define equilibrium, but are insufficient to determine its stability, since they give us no information regarding the behavior of the system when $H \neq H_e$, i.e. when not in equilibrium with the external parameter H_e .

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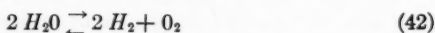
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The peculiar property of G referred to above is as follows

$$\frac{dG}{dt} \begin{matrix} > \\ = \\ < \end{matrix} 0 \text{ according as } H - H_e \begin{matrix} > \\ = \\ < \end{matrix} 0 \quad (41)$$

It will perhaps be well, before proceeding any farther, to illustrate this by a concrete example. Consider the system



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But for our present purposes we are not concerned with the question whether or not the parameters G, H defined for a given system are or are not factors of an energy. We must be prepared to deal with cases where this is either uncertain or actually known not to be true. All we need to know, for our purpose, is that the parameters G, H have the property defined by (41). An example may serve to illustrate the fact that this property may be shared by physical quantities not obviously related to energy.

Among the parameters on which the rate of increase of a human population depends is the area a occupied by them, since this determines the population density, which in turn influences the death rate in well-known manner,⁹ and, presumably, in some degree the birth rate also.

Now there is an obvious relation between population density and ground rent. Regulation is effected about as follows: There is a certain demand for space, a desire for expansion, which may be measured by the rent H per unit area that the individual is willing to pay. On the other hand there is a certain market price H_e which must be paid to obtain accommodation. Now if $H > H_e$, i.e. if, on an average, an individual is willing to pay more than the market price, the population will spread over a greater area by renting more ground. If, on the other hand $H < H_e$ the individual is not willing to pay the market price, he will retrench, he will move from a six room apartment to a five room apartment say, and the area occupied by the population will contract. The parameter H_e functions, in fact, much like a "surface pressure," tending to compress the population into a smaller area. The most striking exhibition of this "surface-pressure" is seen in a great metropolis such as New York, where the population, a naturally two-dimensional structure spread like a film over the earth's surface, has been thrown into great creases towering 700 feet and more, 50 layers deep, above the street level.

⁹ See, for example, Newsholme, *Vital Statistics*, 1899, p. 154.

It will be seen that in this case the internal parameter H and the corresponding external parameter H_e so determine changes in the area a that

$$\frac{da}{dt} \begin{matrix} > \\ < \end{matrix} 0 \text{ according as } H - H_e \begin{matrix} > \\ < \end{matrix} 0 \quad (48)$$

that is to say, the parameters H , a and H_e are related to each other and determine the course of events in a manner analogous to the intensity factor, the capacity factor of an energy, and the "applied force." But it is quite unnecessary to suppose that H and a actually are such factors of an energy in the example cited (population-spread); on the contrary, the writer is opposed to this view, which he has taken occasion elsewhere to discuss.¹⁰ For our purposes it is quite immaterial whether P and a are factors of an energy. All we need know is that they enter into the condition (41) as there set forth.

Condition for Stability toward External Factor. Consider a system for which the condition for equilibrium with the environment is given by

$$\left. \begin{aligned} H &= H_e \\ \varphi(G, H) &= \text{constant} \\ \frac{dG}{dt} &\begin{matrix} > \\ < \end{matrix} 0 \text{ according as } H - H_e \begin{matrix} > \\ < \end{matrix} 0 \end{aligned} \right\} \quad (49)$$

Let

$$\varphi(G, H) = \text{const.}, \text{ i.e. } H = \chi(G) \quad (50)$$

be plotted as ordinates in a rectangular system in which G is plotted as abscissae. Then it is easily shown that the condition for stability of equilibrium is that the curve $H = \chi(G)$ must slope downwards from left to right.

For, suppose it sloped upwards. Let the system be in equilibrium at a point A_1 (Fig. 1), where

$$\left. \begin{aligned} H &= H_1 = H_e \\ G &= G_1 \end{aligned} \right\} \quad (51)$$

Suppose the system is in any way displaced to the point A_2 where

$$H_2 > H_1 \quad (52)$$

$$> H_e \quad (53)$$

¹⁰ "Economic Conversion Factors of Energy," to appear in a forthcoming issue of Proc. Nat. Ac.

Then

$$\frac{dG}{dt} > 0 \quad (54)$$

Hence the point moves along the curve in the direction $A_1 A_2$, i.e. still farther away from equilibrium.

On the other hand, the same reasoning applied to a curve sloping downward from left to right shows that the system after displacement returns to its equilibrium position.

So, for example, the curves representing the relation between pres-

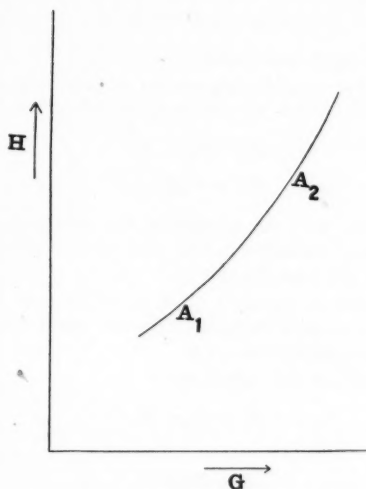


FIGURE 1.

sure and volume of a gas necessarily slope downward from left to right; the same is true of the demand and supply curves of economics. If it were true, as sometimes stated, that the more a man has, the more he wants, economic equilibrium would be an unstable condition.

External Stability and the Principle of Le Chatelier. Consider now a system which obeys the condition

$$\varphi(x, G, H) = 0 \quad (55)$$

$$\left. \begin{array}{l} \frac{dG}{dt} \geq 0 \text{ according as } H - H_e \geq 0 \\ \frac{dG}{dt} \leq 0 \text{ according as } H - H_e \leq 0 \end{array} \right\} \quad (56)$$

Let the system be stable towards H_e both when x is held constant and also when x is at the equilibrium value x_1 defined by

$$\frac{dx}{dt} = f(x_1, G) = 0 \quad (57)$$

This means that all the curves "of constant composition"

$$\left. \begin{aligned} \varphi(x, G, H) &= 0 \\ x &= \text{constant} \end{aligned} \right\} \quad (58)$$

and also the curve "of equilibrium composition"

$$\varphi(x_1, G, H) = 0 \quad (59)$$

slope from left to right downwards.

Now consider two neighboring curves of type (58) (curves of constant composition), which we will suppose solved for H and write

$$H_a = \Psi_a(G, x_a) \quad (60)$$

$$H_b = \Psi_b(G, x_b) \quad (61)$$

Suppose we start with the system in the state represented by the point Q , in internal equilibrium and also in equilibrium with an external parameter H_e (see Fig. 2).

Let x be changed at constant G , so as to increase H according to (55) until $x = x_b$, so that the representative point strikes the second curve of constant composition at R .

Since at the start of this operation

$$H = H_a = H_e \quad (62)$$

and at the end

$$\left. \begin{aligned} H &= H_b \\ &> H_e \end{aligned} \right\} \quad (63)$$

therefore the system is not in equilibrium with the external pressure H_e in the state represented by the point R , but equilibrium (for $x = x_b$) occurs at some other point T which must lie to the right of R along the curve of constant composition RT , since, whenever

$$H > H_e$$

G increases, in accordance with (56).

Furthermore, drawing a horizontal QS , T must lie below S , since the line of equilibrium composition QT must slope from right to left downwards.

It is clear therefore that lines of constant composition are steeper than lines of equilibrium composition.

It follows at once that if G be increased while the system is kept in equilibrium, so that the representative point travels along QT , then the change in x from x_a to x_b is that which at constant G increases H , or at constant H increases G .

But this is the principle of Le Chatelier. This principle therefore holds whenever the conditions (55) (56) are satisfied, and the system

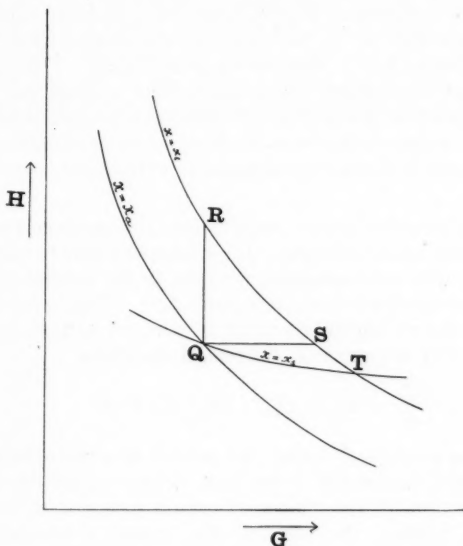


FIGURE 2.

is stable towards H_* both when $x = \text{constant}$ and when $x = x_1$ (i.e. when x has its equilibrium value).

Similarly, it can be shown that if the conditions (55), (56) are replaced by

$$\left. \begin{aligned} \varphi(x, G, H) &= 0 \\ \frac{dG}{dt} &\leq 0 \text{ according as } H - H_* \begin{matrix} \geq \\ < \end{matrix} 0 \end{aligned} \right\}$$

while at the same time the system is stable towards H both when $x = \text{constant}$ and also when $x = x_1$, then the Le Chatelier principle holds. In this case the curves $\varphi(x, G, H) = 0$ (x constant)

and

$$\Psi(x_1, G, H) = 0$$

both slope from left to right upwards, and the curves of constant composition are again steeper than the equilibrium curves. An example of this type is that in which H is temperature and G is heat absorbed by the system (when $H < H_c$, G increases).

Finally, be it remarked that the results here deduced depend solely on *kinetic stability*, i.e. on the fact that the system when displaced from equilibrium has a velocity (rate of change of displacement) towards that equilibrium. The conclusions reached are therefore wholly independent of energetic (thermodynamic) consideration, since no reference whatever has been made to forces or energies or in any way whatsoever to the physical dimensions of the parameters involved.

This completes the present enquiry into the conditions of validity of the principle of Le Chatelier. It remains now only to point out the place which this communication occupies in the general plan of the series of investigations of which it forms part. This series of investigations has for its object the study of material systems evolving in accordance with a system of differential equations

$$\frac{dX_i}{dt} = F_i(X_1, X_2, \dots, X_n; A; P; Q) \quad (65)$$

in which the symbols X denote the masses of certain components S of the system, the symbol A has been written to denote collectively the initial values of the masses of certain components, the P 's are parameters defining the state of the system (extension-in-space, topography, climatic conditions, etc.); and the Q 's are parameters defining the character of the components S .

In a previous communication the kinetics of such a system were studied for the case in which the A 's, P 's and Q 's are constant. This left open for discussion the effect of changes in these parameters. One phase of this subject has been dealt with by the writer elsewhere,¹¹ namely the effect of slow changes in these parameters. The present communication now extends the field of enquiry to the effect of

¹¹ "Note on Moving Equilibria"; to appear in a forthcoming issue of the Proc. Nat. Ac.

changes of any kind in the parameters A or P , with this restriction, it is true, that we have, following Le Chatelier, interested ourselves solely in the ultimate effect upon equilibrium, leaving entirely out of consideration the path by which such equilibrium is reached. In many cases such partial information is of value, the equilibrium being the matter of chief interest, the path of the change of lesser practical importance. Herein lies the utility of such general principles as that of Le Chatelier, of Maupertuis, Lenz and others whose names have become linked with one or other form of reciprocal relations between the parameters defining a state of equilibrium. Since the application of such principles to biological systems has been essayed by various authors, without, however, any rigorous foundation upon which to build, it has appeared to the writer essential, for further progress in this field, to make a critical examination of the basis underlying these principles.

The first part of the book is devoted to a general history of the United States from the discovery of the continent to the present time. It is divided into three volumes. The first volume contains the history of the discovery and settlement of the continent, and the second volume contains the history of the colonies. The third volume contains the history of the United States from the declaration of independence to the present time. The book is written in a clear and concise style, and is well illustrated with maps and portraits. It is a valuable work for the student of American history.

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